PRIMARY AND SECONDARY MINERALS AT THE PADDY'S RIVER MINE, AUSTRALIAN CAPITAL TERRITORY

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ABSTRACT

The partly weathered magnetite-sulphide skarn at the Paddy's River Mine in the Australian Capital Territory contains a diverse assemblage of primary and secondary minerals. More than 70 species have been identified, including excellent specimens of aurichalcite, brochantite, cerussite, hemimorphite, hydrozincite and linarite. Rarer minerals such as caledonite, rozenite, zincsilite and globular native silver also occur at the site.

INTRODUCTION

The Paddy's River Mine, also known as the Cowley copper mine, Congwarra copper lode and the Half Mile deposit, is located along the Paddy's River, 0.7 km south of its junction with the Cotter River in the Australian Capital Territory (Fig. 1). The locality is within easy walking distance (15 minutes) of the Cotter recreational reserve, 22 km west of the capital city of Canberra. The abandoned mine workings are in a magnetite-bearing skarn developed near the contact between a granite body and a limestone unit in the Paddy's River Volcanics. Most of the magnetite outcrops are on the eastern side of a steep and partly timbered ridge. In addition to magnetite, the skarn contains small quantities of copper, lead, zinc, silver and gold, and the deposit was worked on a small scale for some of these metals at the turn of the century. Today the old mine is a favourite collecting site for amateur mineralogists, as well as an important locality for school and college excursions. The dumps and outcrops contain a variety of skarn minerals and primary sulphides, plus a host of interesting and rare secondary minerals. To date, only a very brief description of the deposit has been published (Smith, 1963) and there has been no systematic identification or description of the great variety of mineral species.

HISTORY

The Paddy's River deposit was first prospected and worked by Thomas Coyle in 1895. Coyle mined 61 tonnes of ore for a production of 2.6 tonnes of copper and 26.1 kg of silver, worth at the time £225 (N.S.W. Mines Dept. 1896, Gilligan, 1975).

In 1897 copper prospecting operations were resumed by members of a Melbourne financed syndicate, who were said to have obtained "fair prospects", although there is no record of production at this time (N.S.W.

Glossary

- SKARN thermally metamorphosed limestone or dolomite, characterised by the presence of minerals; often sulphides.
- TUFFS (= pyroclastic rocks) from volcanic eruptions.
- SILURIAN geological period 435 - 395 MY ago.
- EPIDOTES rock forming silicate minerals
- ADAMELLITE form of granite w/- %'s calcium & potassium in equal amounts.

Dept. Mines, 1898).

No further prospecting or mining activity was reported until 1907 when the Cowley Copper Syndicate Ltd. extensively tested the deposit. This group, headed by a Mr. P.E. Marmion of Queanbeyan, extended the existing adit (Tunnel No. 1) and developed two additional adits (Tunnels No. 2 and 3) together with a number of cross cuts and winzes (Marmion, 1909; Figs. 1, 2 and 3). The results of this work were generally disappointing. Some good patches of ore were encountered but could not be proved into a payable deposit and the mine was closed down. The N.S.W. Mines Department (1909a and 1909b) reported that the syndicate had "proved the existence of a large low-grade ore deposit, but of too complex a nature to permit of cheap treatment" and that "no ore was despatched from the mine owing to its somewhat inac-

cessible location and the low grade of the material".

In 1910, prior to the construction of Canberra, the area was included in the newly constituted Federal Capital Territory for which annual mining reports were not furnished. Consequently there is little information available for the period up until the 1940's. However, it appears that there was no major mining or prospecting activity at the locality. In 1946 Broken Hill South Ltd. applied for a mining lease over the area and the deposit was mapped and sampled by the Bureau of Mineral Resources. Detailed sampling was carried out along the southern adit (Tunnel No. 2) and assay results reported (see Table 1). These results were not sufficient to encourage further work at this time.

In 1951 the deposit was inspected by Lake George Mines Pty. Ltd. with a view to

possibly mining the copper-bearing ore for treatment in their plant at the large Captain's Flat copper-lead-zinc mine, 58 km southeast of Canberra. This was not followed up, partly because of the difficulty in obtaining an authority for further exploration and mining in the A.C.T. (Glasson, 1951; and pers. comm., 1986). At one time, probably also in the 1950s, the deposit was investigated by the N.S.W. Joint Coal Board as a potential source of magnetite for coal washing (Smith, 1963). In 1960 surface outcrops were sampled by the Bureau of Mineral resources and tested for their iron and silica content (Smith, 1963; Table 1). The deposit is estimated to contain about one million tonnes of magnetite.

The Paddy's River mine is now abandoned and it is highly unlikely that any further prospecting or mining activity will be permitted at the site due to its close proximity to the Cotter Reserve and Canberra's water supply catchment. The locality has also been placed on the registry of geological monuments for the A.C.T. because of its significance as an educational and collecting site. Amateur groups, including the Canberra Gem Society and the A.C.T. Lapidary and Mineral Club have collected at the site over many years and some members of these organisations have built up extensive collections, particularly of micromount samples. A comprehensive collection of minerals from the site is held by the authors and some material is kept in the Geology Museum at the Canberra College of Advanced Education. The Bureau of Mineral Resources in Canberra also has a small suite of samples from the mine including samples of linarite and magnetite. Some large samples can still be obtained at the site by digging into the dumps, but the best material is of micromount size. This includes delicate and intricate secondary mineral intergrowths and crystals of excellent quality. At the present time restricted collecting from the dumps and outcrops is permitted. Most of the old underground

workings are inaccessible and should not be entered as they are in a highly dangerous condition.

GEOLOGY AND NATURE OF THE SKARN

Detailed mapping by the authors around the old mine has revealed a magnetite-rich, replacement skarn, formed where coarse-grained granite of the Shannon's Flat Adamellite has intruded a limestone body within Mid to Late Silurian, dacitic tuffs (Fig. 1; Owen and Wyborn, 1979). The skarn shows many of the features characteristic of classic skarn deposits, including zoning away from the granite contact (cf. Rose and Burt, 1979). It consists of a number of irregular, magnetite-rich bodies which contain abundant quartz veins and epidote-quartz rocks close to the granite. These grade out into a zone of mixed magnetite and silicate skarn. This in turn is surrounded by a narrow zone of predominantly silicate skarn containing irregular masses of hedenbergite-, actinolite-, chlorite- and epidote-rich rocks. Sulphide minerals, which are the primary source of the various base metals and silver, occur as veins and disseminations in magnetite and mixed skarn near the outer contact of the magnetite-rich part of the deposit. The various sulphide minerals are complexly intergrown on a fine scale. To the north, the silicate skarn is succeeded by marble and partly recrystallized limestone. Areas of tuff separate some of the magnetite bodies, particularly at the southern end, suggesting replacement of irregular limestone lenses interbedded with these volcanics. Some of the tuffs also appear to have been replaced by skarn. Maximum surface dimensions of the skarn are 400 m by 170 m and the main magnetite body extends to at least 90 m below the surface.

The host volcanics and limestone dip steeply to the east (ca. 70°-80°) and show some cleavage development. Fine to medium grained lithic-crystal tuffs underlie,

Fig. 2. Part of the old surface workings at the Paddy's River Mine (foreground) also showing the dump from Tunnel No. 1 (downhill and behind P. Millsteed). The large outcrop in the foreground is gossan replacing magnetite skarn. Photograph taken looking east.

* density magnetite = 5.2 ; also called 'lodestone', black, Mohs 5.5-6.5

10^6 tons water $\equiv$ cube, side 10^2 m.

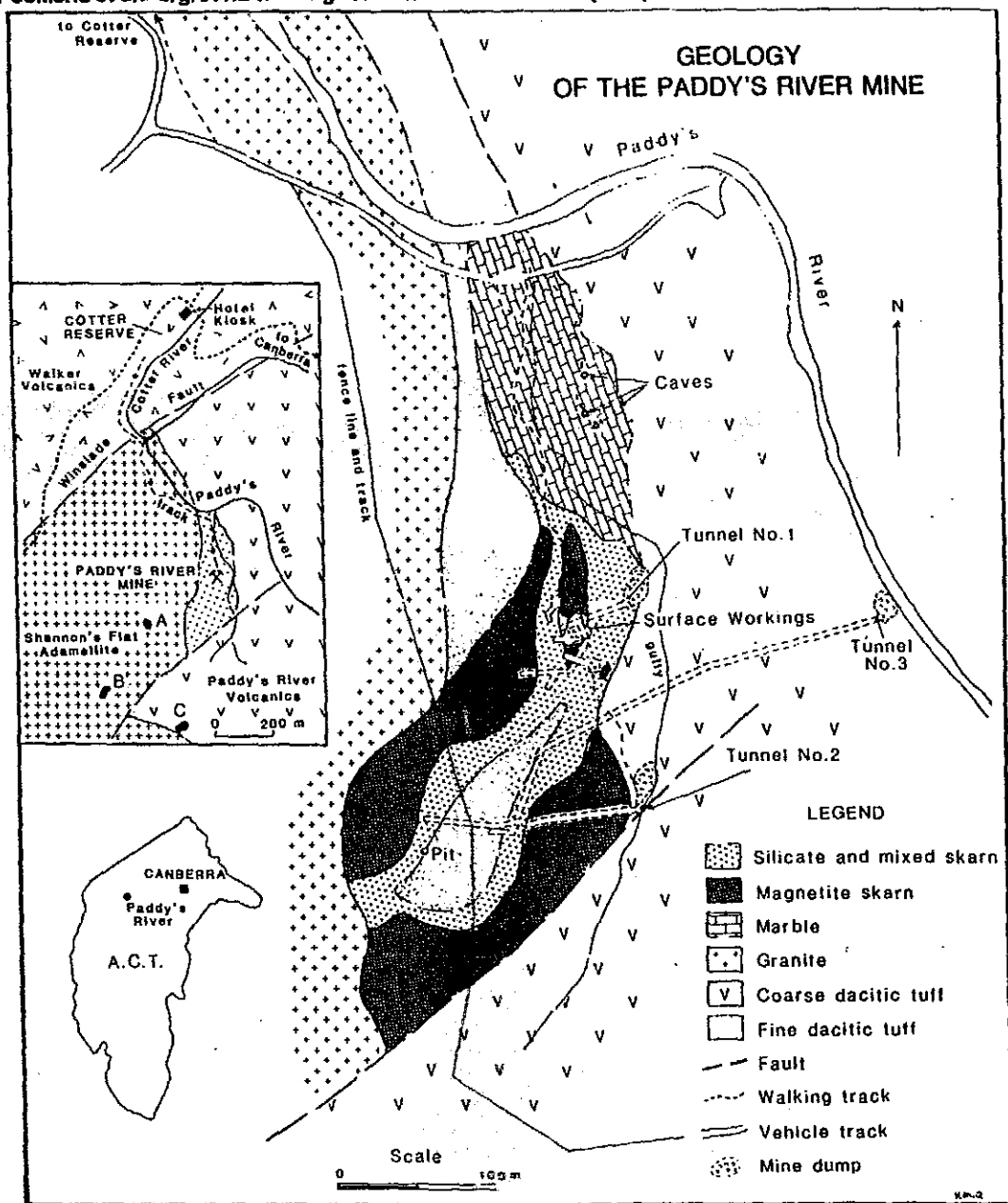$\Rightarrow 10^6$ tons magnetite $=$ cube, side $\sqrt[3]{(10^6/5.2)} \simeq 57.7$ m.

$Fe_3 O_4$.

and are interbedded with the limestone, which in turn is overlain by a thick body of coarse grained crystal-lithic tuff. The southern end of the deposit is terminated against these coarse grained tuffs by a north-east trending fault. This fault has laterally dis-placed the granite contact by approximately 300 m to the west on the southern side.

Three very small satellite bodies of magnetite-rich skarn also occur in the vicinity of the main deposit (Fig. 1). Two of these are developed within granite and may repre-

Fig. 1. Location of the Paddy's River Mine and detailed geology of the skarn deposit. Outcrops labelled A, B, and C (in the main insert map) are the small satellite skarn bodies referred to in the text. Positions of underground workings are taken from Marmion (1909).

GEOLOGY
OF THE PADDY'S RIVER MINE

LEGEND

Silicate and mixed skarn
Magnetite skarn
Marble
Granite
Coarse dacitic tuff
Fine dacitic tuff
Fault
Walking track
Vehicle track
Mine dump

sent small roof pendants or rafts of material that were engulfed by the intruding granite.

Weathering and solution of the marble north of the main skarn deposit has produced several small caves (Fig. 1). Some interesting minerals are developed in pellets, lumps and bedded material in cave-floor sediments and in speleo-forms. Minerals identified include alunite ($KAl_3(SO_4)_2(OH)_6$), aragonite ($CaCO_3$), berlinite ($AlPO_4$), collophane ($Ca_5(PO_4,CO_3)_3(OH)$), crandallite ($CaAl_3(PO_4)_2(OH)_5.H_2O$), dahllite ($Ca_5(PO_4,CO_3)_3(OH)$), francoanellite ($H_6(K,Na,NH_4)_3Al_5(PO_4)_8.13H_2O$), gypsum ($CaSO_4.2H_2O$), huntite ($CaMg_3(CO_4)_4$), hydromagnesite ($Mg_5(CO_3)_4(OH)_2.4H_2O$), leucophosphite ($KFe_2(PO_4)_2(OH).2H_2O$), nesquehonite ($Mg(HCO_3)(OH).2H_2O$) niter ($KNO_3$) and nitrocalcite ($Ca(NO_3)_2.4H_2O$) (Table 2). Some of the cave deposits appear to have been mined, probably for use as fertilizer.

PRIMARY MINERALS

Primary or hypogene minerals identified at the Paddy's River deposit are listed in Table 2, together with the relevant techniques used in identification. The most abundant skarn minerals are magnetite, epidote, chlorite, hedenbergite, actinolite, quartz, calcite, grossular, andradite, and diopside. There are also other silicates in lesser abundance. The main sulphide minerals are sphalerite, galena, chalcopyrite and pyrite. Minor sulphides include arsenopyrite, acanthite and bornite.

Silicates
Actinolite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$

Pale to dark green actinolite occurs in asbestiform and radiating fibrous masses in layers and pods up to 50 cm wide. These masses mostly occur around, and close to the magnetite bodies, particularly in the area of the old surface workings. Actinolite also occurs intergrown with magnetite, chlorite, epidote and sulphides.

Andradite $Ca_3Fe_2(SiO_4)_3$

Andradite has been observed as green and yellow-brown, massive aggregates and individual dodecohedrons up to approximately 1 cm in diameter. It is mostly found in magnetite-rich skarn in association with magnetite, quartz, calcite and chlorite. Three analysed grains showed an average of 74% of the andradite molecule ($Al_4An_{74}Gr_{20}Sp_2$).

Chlorite Group $(Al,Fe,Mg,Mn)_{5-6}(Al,Fe,Si)_4O_{10}(OH)_8$

A range of optically and compositionally distinct chlorite minerals occurs in the skarn, mostly in association with epidote and actinolite, but also in minor amounts with magnetite and the various garnets. Fine grained epidote-chlorite rocks with a serpentinite-like appearance are a feature of the outer parts of the skarn. Minor chlorite also occurs in marble and as an alteration product of mafic minerals in the enclosing tuffs. Chlorite minerals identified in unweathered rocks include ferroan clinochlore, leuchtenbergite, gonyerite, thuringite and an 11B chlorite.

Clinozoisite $Ca_2Al_3(SiO_4)_3(OH)$

Acicular grains of clinozoisite up to several centimeters long have been noted in bunches in some of the silicate- and magnetite-bearing skarns.

Dannemorite $Mn_2(Fe,Mg)_5Si_8O_{22}(OH)_2$

Dannemorite has been identified as small greyish-green needles and fascicular grains intergrown with actinolite and calcite in amphibole-rich skarn.

Diopside $CaMgSi_2O_6$

Pale green diopsidic skarns occur in several areas close to the main magentite bodies. Diopside is usually associated with quartz, minor calcite, sulphides and magnetite. Microprobe analysis of two diopside grains indicated 83% of the $CaMgSi_2O_6$ molecule.

Epidote $Ca_2(Al,Fe)_3(SiO_4)_3(OH)$

Epidote occurs widely in fine grained aggregates with quartz, chlorite, grossular and calcite. It also occurs as a minor mineral, intergrown with magnetite and hedenbergite. Some quartz-epidote rocks and veins contain epidote crystals up to 1 cm long.

Grossular $Ca_3Al_2(SiO_4)_3$

Grossular is found as small, usually dull red, subhedral grains and trapezohedrons (up to 2 mm), associated with calcite and magnetite. Analyses of several grains indicated an average of 68% of the grossular end member ($Al_6An_{17}Gr_{68}Sp_9$).

Hedenbergite $Ca(Fe,Mn)Si_2O_6$

Dark green and dense skarn rocks rich in hedenbergite occur in irregular outcrops around the magnetite bodies. The hedenbergite forms aggregates of interlocking prismatic grains (up to 3 mm) with intergranular quartz, carbonate and epidote. In thin section, hedenbergite shows replacement by calcite and small magnetite-hydrogrossular aggregates. Energy dispersive analysis by electron microprobe indicated an iron-rich variety.

Hydrogrossular $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$

Hydrogrossular appears to be a late-stage silicate in the skarn, commonly replacing other minerals or occurring in cross-cutting veins with calcite. Crystals up to .5 mm in diameter have been noted in calcite veins in magnetite.

Quartz SiO_2

Fine grained quartz occurs throughout the magnetite and silicate skarns, and in some assemblages it is a major component. Veins of milky, crystalline quartz are common in massive magnetite close to the granite contact and crystals up to 4 cm long have been noted. Quartz also occurs in late-stage veins with calcite and hydrogrossular.

Talc $Mg_3Si_4O_{10}(OH)_2$

Small masses of pale green to white talc

Fig. 3. Entrance to the upper adit (Tunnel No. 2) at the Paddy's River Mine. This adit was developed by the Cowley Copper Syndicate between 1907 and 1909. Rocks to the left of the entrance are coarse grained tuffs of the Paddy's River Volcanics.

Fig. 4.Prismatic crystals of linarite (up to 2.2 mm) with hemimorphite.

Fig. 5. Twinned cerussite crystal 0.5 mm on hemimorphite with surrounding "sturtite".

Fig. 6. Aggregate of native silver on smithsonite, also showing radiating crystals of aurichalcite.

occur in association with dolomite and magnetite in altered amphibole-rich rocks at one of the small satellite skarns (satellite B). Talc is also found in weathering residues after marble near the main deposit.

"Uralite"

Uralitized pyroxenes occur in some of the silicate skarn.

Sulphides
Acanthite Ag_2S

Some small, greenish-grey prismatic grains contained in galena and observed in polished section have been identified as acanthite. This appears to be the main silver mineral in the sulphides and is usually present in only trace amounts.

Arsenopyrite FeAsS

Arsenopyrite is a minor mineral in the sulphide lodes. It also occurs as inclusion in magnetite-rich material, generally as microscopic euhedral grains.

Chalcopyrite $CuFeS_2$

Chalcopyrite is widely distributed throughout the sulphide-rich parts of the skarn, occurring in at least minor amounts in most sulphide samples. It is present as irregular intergrowths with magnetite, sphalerite, galena, actinolite and chlorite, and forms inclusions in sphalerite and euhedral grains of magnetite. It also occurs with pyrite in cross-cutting veinlets. Some chalcopyrite-rich patches of ore contain irregular aggregates of chalcopyrite up to several centimetres across. Minor bornite was detected during X-ray diffraction studies of one of these large chalcopyrite masses. Chalcopyrite shows minor alteration to sooty chalcocite and covellite.

Galena PbS

Galena typically occurs as disseminated, wispy grains and aggregates (0.02 to 2 mm) intergrown with actinolite, magnetite and other sulphides. It is commonly associated with sphalerite but also occurs as microscopic inclusions in chalcopyrite. It contains inclusions of chalcopyrite, sphalerite, acanthite and rare tiny grains (<2 u) of a bright yellow-white mineral, tentatively identified as electrum. Coarser grained galena has been noted in calcite veins cutting magnetite.

Pyrite FeS_2

Pyrite is not an abundant mineral but occurs in trace amounts in most sulphide samples. It mostly forms small aggregates of subhedral grains (to 0.2 mm) intermixed with the other sulphides, but also occurs in cross-cutting veinlets and coarse grained masses in magnetite and chlorite. Pyrite cubes up to several centimetres across have been found in highly chloritic rocks at the deposit. Some pyrite contains inclusions and veinlets of other sulphides including galena and digenite (Cu_9S_5).

Sphalerite (Zn,Fe,Mn)S

Sphalerite is the most common sulphide at the deposit and occurs in fine grained, irregular aggregates intergrown with other sulphides and with silicates, particularly actinolite. Most sphalerite examined in polished section contained numerous tiny inclusions of chalcopyrite, generally referred to as "chalcopyrite disease". This is possibly a replacement or exsolution feature of chalcopyrite after sphalerite (cf. Craig and Vaughan, 1981, p.125). Microscopic inclusions of galena and subhedral magnetite also occur in sphalerite. Rarely sphalerite has been observed as transparent honey-yellow plates and translucent, brownish-red pseudo-octahedral crystals up to 0.4 mm across (G. Morvell, pers. comm.). Sphalerite below the oxidized zone shows minor replacement by supergene covellite (CuS).

Oxides
Magnetite Fe_3O_4

Magnetite generally occurs in massive or fine granular form, in places associated with quartz, andradite, chlorite, grossular and epidote. There are three main types of magnetite: an early formed massive and granular variety, magnetite intergrown with sulphides and specular hematite, and a fine-grained variety in magnetite-hydrogrossular intergrowths after hedenbergite. Magnetite crystals can be found in veins and quartz-rich pods. These include dodecohedra up to 3 cm in 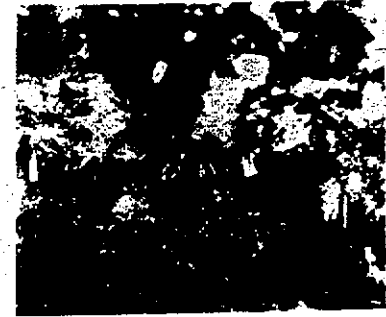diameter and smaller octahedral crystals. Well developed octahedral crystals (to 3 mm) have been found in one of the small satellite bodies (satellite C).

Specular Hematite Fe_2O_3

Most hematite at the deposit is secondary in origin, having formed from the near surface oxidation of magnetite. However, some bladed, specular hematite occurs intergrown with primary silicates, magnetite and sulphides and as tiny inclusions in fresh sulphides indicating that is probably of primary origin.

Carbonates
Calcite $CaCO_3$

Calcite is the main constituent of the marble and limestone in the area, forming small interlocking and recrystallized grains (mostly less than 0.1 mm). Pods of marble preserved within magnetite show coarser grain size. Calcite also occurs in the matrix of some silicate skarn rocks and as secondary veins in marble and magnetite skarn. Some calcite films and veins on magnetite fluoresce red, suggesting a manganoan variety.

Dolomite $CaMg(CO_3)_2$

Dolomite is found in buff-coloured secondary veins and thicker "layer-cake" beds cutting marble. It also occurs as crystals up to 6 mm long near the contact between

Fig. 7. Rosette of tabular hemimorphite crystals 1.25 mm encrusting "sturtite".

skarn and enclosing tuff.

Sulphates
Barite BaSO$_4$

Small veins of translucent, pale brown barite occur in some of the tuffs adjacent to the skarn deposit.

SECONDARY MINERALS

A large number of secondary minerals are developed in the upper, weathered and oxidized part of the sulphide-bearing magnetite outcrops (Table 2). The oxidized zone appears to be very irregular and in some areas fresh sulphides are preserved almost at the surface. Heavily oxidized material consists mainly of mixed magnetite and hematite with patches of porous and botryoidal limonite. Other secondary minerals occur as encrustations, coatings, veins and stalactitic masses in cavities, joint fractures and pipes in the oxidized magnetite and surrounding mixed magnetite-silicate skarn. Important and well developed secondary minerals include hemimorphite, cerussite, linarite, brochantite, hydrozincite, anglesite and aurichalcite. The best examples of these minerals occur on the dumps and outcrops associated with the shallow surface workings above Tunnel No. 1 (Figs. 1 and 2).

Native Elements
Silver Ag

A single specimen containing a small (0.4 mm across) encrusting aggregate of native silver was collected from the main surface dumps several years ago by Mr. G. Morvell of Canberra. The native silver occurs in a small cavity in partly oxidized sulphide material and consists of clusters of minute spheroidal globules (Fig. 14). Further checking revealed traces of native silver as small grain clusters in some oxidized chloritic skarn at the main deposit and in talc-magnetite rocks at the satellite B locality.

Sulphur S

Small amounts of native sulphur have been chemically detected in limonitic material from the oxidized zone. Pale coloured, orthorhombic crystals of native sulphur (less than 0.2 mm) have also been directly observed lining small cavities in oxidized sulphides. These appear to be quite rare.

SILICATES
Chrysocolla (Cu,Al)$_2$H$_2$Si$_2$O$_5$(OH)$_4$.nH$_2$O

Chrysocolla occurs as amorphous, translucent blue coatings in oxidized material at the main surface workings. It has also been noted as tabular pseudomorphs after hemimorphite (G. Morvell, pers comm.)

Clay Minerals and Secondary Chlorites

A variety of clay and chlorite minerals have formed from the surface weathering of exposed silicate skarn. Minerals identified include: Meta-halloysite, illite, Cu-bearing smectites, nontronite, sauconite, and chamosite.

Hemimorphite Zn$_4$Si$_2$O$_7$(OH)$_2$.H$_2$O

Hemimorphite is widely distributed in the oxidized zone at the main deposit and associated satellite bodies, occurring as coatings in cavities and in rich, pipe-like masses up to tens of centimetres in diameter. It forms small, globular, spherical or hemispherical aggregates (up to 1 mm), clusters of tiny, tabular crystals (up to 3

mm), white to brown crystal crusts and very fine grained, white or grey, massive fillings (Figs 7 and 13). It is generally developed on goethite, pyrolusite and amorphous iron and manganese oxides and is commonly associated with linarite, brochantite, cerussite, malachite, hydrozincite and aurichalcite.

Inesite Ca$_2$Mn$_7$Si$_{10}$O$_{28}$(OH)$_2$.5H$_2$O

Tiny pale grey prisms of inesite have been found with hemimorphite where this mineral forms pipe-like concentrations.

Opaline Silica (Hyalite)SiO$_2$.nH$_2$O

Opaline silica occurs in parts of the main gossan as thin veinlets and glassy globules in cavities and fractures. X-ray studies indicate that this material is mainly hyalite but some of the opal contains a cristobalite-tridymite mixture.

Zincsilite Zn$_3$Si$_4$O$_{10}$(OH)$_2$.4H$_2$O

A soft pale brown mineral mixed with hemimorphite from one of the small satellite bodies (satellite B) has been identified as zincsilite.

OXIDES AND HYDROXIDES
Carphosiderite
(Hydronium Jarosite) (H$_3$O)Fe$_3$(SO$_4$)$_2$(OH)$_6$

Carphosiderite occurs as bright yellow, powdery coatings on hematite and magnetite surfaces in the oxidized zone.

Ferrihydrite 5Fe$_2$O$_3$.9H$_2$O

An orange-brown sludge can be seen forming at the present time near seepages at the base of some slopes near the mine workings. Chemical analysis indicates that this material contains ferrihydrite.

Goethite FeO(OH)

Goethite and associated earthy hematite are the main constituents of gossanous material developed on the oxidized magnetite bodies. The goethite includes both residual and exotic (redistributed) varieties and parts of the gossan show a well developed cellular boxwork structure of limonite (mostly goethite) after magnetite.
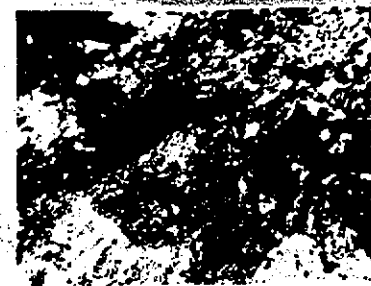
Hematite Fe$_2$O$_3$

Fig. 8. Striated crystals of brochantite to 0.15 mm on limonite with associated carphosiderite.

Coatings and vug fillings of powdery, red-brown hematite are common in oxidized magnetite outcrops. Earthy hematite is also common in the soil overlying weathered magnetite. Secondary, specular hematite occurs in cavities in magnetite and in weathered silicates. Dense hematite (martite) has extensively replaced magnetite in the oxidized zone and replacement textures can be clearly seen in polished section. Blood-red, powdery coatings on some gossan surfaces probably represent hydrated hematite or "turgite". Considerable water is lost from this material on heating above 140°C.

Pyrolusite MnO^2

Black coatings of pyrolusite occur on weathered silicate skarn and with some hemimorphite concentrations.

Todorokite (Mn,Ca,Mg)Mn$_3$O$_7$.H$_2$O

Todorokite is widely distributed in the oxidized zone as brown botryoidal coatings. It is also commonly associated with hemimorphite, forming an underlayer for crystals of this mineral.

"Sturtite"

A lustrous dark brown material is common as thick coatings and small botryoidal masses in vugs and cavities in association with goethite and pyrolusite. Crystals and aggregates of hemimorphite, brochantite, linarite and other sulphates are typically de-

Fig. 9. Radiating cluster of acicular aurichalcite crystals developed on "sturtite". Group is 1.75 mm in diameter.

veloped on this material. On the basis of X-ray diffraction studies and chemical tests indicating a high manganese content, this substance has been identified as "sturtite". "Sturtite" is well known from the oxidized zone of the Broken Hill orebody in N.S.W., but is not recognized as a definite mineral species (Fleischer, 1983).

"Wad"

Black, earthy veins and patches of "wad" (mixed manganese oxides and hydroxides with some iron) occur in gossan after massive magnetite. Some of this material contains up to 24% manganese, traces of cobalt and up to 700 ppm silver.

HALIDES

Cerargyrite AgCl

Ammonia-soluble silver chloride occurs widely in earthy gossanous material from the main workings and the satellite B deposit. At the latter locality crystalline cerargyrite has been detected as tiny bunches of pale purple cubes (less than 0.02 mm) lining cavities in limonite. Some of the silver chloride may also be present as the amorphous or colloidal form sometimes referred to as "ostwaldite" or "butter milk" silver (e.g. Cornu, 1909).

CARBONATES

Aurichalcite $(Zn,Cu)_5(CO_3)_2(OH)_6$

Aurichalcite is widely distributed in small amounts, occurring as pale blue crusts, aggregates of needle-like crystals and larger prismatic crystals up to 3 mm long. It is developed in association with cerussite and hemimorphite at the main surface workings, and as coatings on hemimorphite associated with smithsonite at the satellite B skarn. Tiny, delicate sets and clusters (up to 1 mm) of acicular aurichalcite are among some of the more attractive specimens from the locality (e.g. Fig. 9).

Cerussite $PbCO_3$

Cerussite occurs in a variety of forms including small, grey to colourless tabular crystals (up to 3 mm), greenish hairs (up to 45 mm), discoidal grains coating cavity surfaces and white asbestiform masses in limonite. Twinned crystals are not uncommon (Fig. 5). Green-, pale blue- and brown-stained varieties also occur in crusts and stringers. In some parts of the oxidized zone cerussite is enriched in greyish-white pods up to 40 cm across. Cerussite is commonly associated with linarite as well as minor brochantite and anglesite. It occurs on hemimorphite and some cerussite crystals show coatings of linarite and anglesite.

Hydrozincite $Zn_5(CO_3)_2(OH)_6$

Hydrozincite occurs in some drusy linings to cavities in goethite, where it may form fine specimens of crystals up to several millimetres. It can be found associated with calcite and epidote and also as coatings on some marble. The mineral fluoresces brilliant blue-white.

Kutnahorite $Ca(Mn,Mg,Fe)(CO_3)_2$

Brown, fine granular material in hemimorphite pipes at the small satellite B locality has been identified as kutnahorite.

Malachite $Cu_2(CO_3)(OH)_2$

Malachite is relatively uncommon in the oxidized zone at Paddy's River. It has been noted as minor earthy crusts and small spheroidal aggregates of acicular grains (Fig. 11). It occurs in dump material at the main surface workings and in a small pit on the western side of the main deposit. It is generally associated with cerussite pods and lumpy goethite.

Siderite $FeCO_3$

Dark brown rhombs of siderite (crystals up to 0.5 mm) occur with quartz, hematite and hemimorphite at the small satellite B deposit. Tiny siderite rhombs (less than 0.1 mm) have also been observed lining cavities in oxidized silicate skarn at the main deposit.

Smithsonite $ZnCO_3$

Smithsonite occurs rarely as white and pale, greenish-grey encrustations in cavities, either alone or with hemimorphite. Colourless, tear-drop, crystal aggregates and small rhombohedral crystals up to 0.2 mm have also been observed. Pale green translucent aggregates of smithsonite have been noted in association with native silver and hemimorphite in one sample.

SULPHATES

Anglesite $PbSO_4$

Anglesite is found as small colourless prisms (up to 3 mm) and as very fine grained coatings in cavities. It is associated with cerussite, brochantite and linarite.

Brochantite $Cu_4(SO_4)(OH)_6$

Brochantite is the predominant, green secondary mineral found at the Paddy's River deposit. It mostly occurs as small granular lumps and coatings of tiny acicular grains (up to 0.2 mm) in cavities and on fracture surfaces in magnetite, limonite and weathered silicate material. Well developed, prismatic and stubby, striated crystals (to 2 mm) occur in some material from the main dumps (Fig. 8). Brochantite is commonly associated with linarite and hemimorphite and has also been observed encrusting and possibly replacing malachite (Fig. 11).

Caledonite $Pb_5Cu_2(CO_3)(SO_4)_3(OH)_6$

Rare caledonite occurs as minute aqua-blue, prismatic crystals up to 0.05 mm across. These crystals are striated parallel to the prism faces and are commonly associated with white coatings of zinc sulphates.
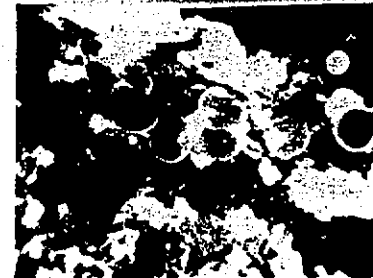
Copiapite $(Fe,Mg)Fe_4(SO_4)_6(OH)_2.20H_2O$

Fig. 10. Spheroidal malachite aggregates to 0.4 mm associated with cerussite.

Copiapite occurs as yellowish, microcrystalline coatings and brown patches of hard gritty material on magnetite-hematite surfaces.

Goslarite $(Zn,Mn)SO_4.7H_2O$

Goslarite has been detected as a component in white to pale green efflorescent coatings on oxidized surfaces.

Gypsum $CaSO_4.2H_2O$

Minor gypsum occurs as fine-grained crystalline crusts, aggregates of parallel crystals (up to 9 mm long) and small lumps in weathered mullock on the mine dumps.

Jarosite $KFe_3(SO_4)_2(OH)_6$

Dark-yellow aggregates of small jarosite crystals have been observed on irridescent limonite in specimens of tremolite-magnetite rock. This mineral also forms powdery coatings on some of the old underground mine surfaces.

Langite $Cu_4(SO_4)(OH)_6.2H_2O$

Langite forms blue-green crusts and is mostly found coating diopside grains in weathered sulphide-silicate skarn. It also occurs mixed with brochantite.

Linarite $PbCu(SO_4)(OH)_2$

Linarite is a widespread secondary mineral in the oxidized zone. It typically occurs as fine grained, blue coatings on limonite, as well as in scaley aggregates on limonite, as well as in fractures in actinolite-rich silicate skarn. Less commonly it forms small (to 2 mm), azure
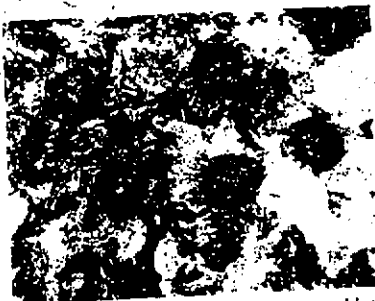
Fig.11.Malachite coating and pseudomorphing brochantite on hemimorphite with intergrown linarite. Malachite aggregates are 0.5mm across.

blue prismatic crystals lining cavities with cerussite, anglesite and brochantite (Fig. 4). Rarely, linarite can be found in radiating prisms up to 1 cm long.

Pickeringite $MgAl_2(SO_4)_2 2H_2O$

White fibres of pickeringite have been detected in efflorescent coatings on a piece of buried chlorite-talc-magnetite-quartz rock from the dump at the satellite B deposit.

Rozenite $FeSO_4.4H_2O$

Rozenite has been identified in soluble white crusts on some surfaces of oxidized material.

Zinc Sulphates

Various zinc sulphates occur in fine, dusty white coatings and films developed on less exposed surfaces in the old pit and on lumps of sulphide ore buried in the dumps. The major components are goslarite (see above), bianchite (Zn $(SO_4).6H_2O$)and a basic zinc sulphate-hydrate ($Zn_7(OH)_{12}SO_44H_2O$) which is insoluble at pH greater than 5.3. Chemical analysis of soluble material indicates that it contains in addition to major Zn, minor Al, Mg, Na, Cu, Cd, K and Mn, largely as sulphates.

PHOSPHATES

Pyromorphite $(Pb,Ca)_5(PO_4)_3Cl$

Trace pyromorphite occurs as pale yellowish-green, earthy coatings and mamillary crusts in bog-ork limonite. Semi-quantitative chemical anlysis of some separated pyromorphite indicated major Pb, Ca and P with minor Cl and As. Yellow-brown to white translucent fibres associated with this pyromorphite were found from X-ray diffraction studies and chemical analysis to be carbonate-hydroxyl apatite. Generally phosphates appear to be very rare in the oxidized zone.

ARSENATES

Scorodite $FeAsO_4.2H_2O$

Scorodite has been detected as coatings on some weathered sulphide samples buried in the lower dumps. It occurs as pale, resinous brown globules and cup-like aggregates from 100-400µ across. Micro-probe analysis indicated trace impurities of Mn and Zn.

DISCUSSION

The skarn mineralisation at Paddy's River formed by metasomatic alteration of limestones interbedded with dacitic tuffs during intrusion of the nearby Shannon's Flat Adamellite. Radiometric dating of this intrusion near Paddy's River using the rubidium/strontium technique, has indicated an emplacement age of 414±2 million years (Roddick and Compston, 1976, adjusted using decay constant of Steiger and Jager, 1977). This would give a maximum possible age for the skarn mineralization of about 416 million years.

Mineralogical variation in the skarn is related partly to distance from the granite contact and partly to original host rock composition. For example, chlorite- and epidote-rich rocks appear to be more common in peripheral silicate skarn where the skarn is flanked by tuffs. Hedenbergite-rich assemblages occur adjacent to marble. Factors which are generally thought to be important in controlling skarn mineralogies include: chemical composition of the original rocks and introduced fluids, pressure, temperature, redox potential and pH (acidi-

ty-alkalinity) of the environment and fluids. It is difficult to interpret with certainty the complex physical and chemical conditions of skarn formation at Paddy's River, particularly as there has been some later (retrograde?) alteration of certain mineral assemblages. The mineralizing fluids are likely to have contained significant iron, to account for the abundant magnetite and iron-rich silicates, such as hedenbergite and actinolite. They were probably also CO_2-rich as a result of decarbonation reactions in the limestone. The presence of sulphides would require a moderate sulphur activity, at least in the later stages of skarn development. By analogy with similar skarn deposits, fluids containing base metals and silver were probably introduced from the intruding granite, (cf. Shimazaki, 1980), although the possibiity of leaching from the surrounding volcanics can not be ruled out on existing evidence. The presence of epi-

Fig. 12. Radiating, acicular linarite crystals (6 mm) developed on ferruginous, weathered tremolite-rich skarn.P. Millsteed specimen and photo.

dote-quartz rocks and primary hematite, together with the general abundance of epidote and magnetite, indicates a relatively high oxygen fugacity throughout much of the skarn during its formation (cf. Liou, 1973).

Some broad limits can be placed on peak temperature conditions in the skarn by cautious application of experimental mineral equilibria data, assuming pressures during contact metamorphism of approximately 1 kb (±0.5 kb). Given that the host limestone would act as a rather weak rock, fluid pressures would probably have approximated total pressure. This pressure estimate is based on petrographic features of the Shannon's Flat Adamellite together with contact relationships suggesting that it is a high level intrusion (Roddick and Compston, 1976). The fact that the granite is emplaced into comagmatic volcanics of only slightly older age and with a stratigraphic thickness of about 4 km (Owen and Wyborn, 1979) would lend further credence to this estimate. Absence of wollastonite in calcite-quartz, hedenbergite and grossular-quartz assemblages indicates that temperatures in the skarn were less than an absolute maximum of 670°C and probably less than 600°C, depending on the exact pressure and activity of CO_2 (Greenwood, 1967, Winkler, 1979). Formation of andradite in sulphide free, quartz-calcite-magnetite rocks, suggests that temperatures exceeded 500°C for likely conditions of CO_2 activity (Taylor and Liou, 1978). Diopside-bearing assemblages would be consistent with temperatures of about 450°C at 1 kb pressure (Slaughter et al. 1975).

Textural and mineralogical features in the skarn indicate early formation of calc-silicates and massive magnetite, with chloritic and actinolitic rocks developing around the magnetite bodies, possibly at a later stage. Veining and small scale cross-cutting textures indicate that sulphides, some specular hematite and additional

magnetite were introduced into pre-existing silicate and magnetite skarn rocks. It is difficult to determine a paragenetic sequence for the sulphides. Sphalerite, chalcopyrite, galena and pyrite generally show mutual intergrowth and appear to have deposited at approximately the same stage. There has possibly been some replacement of sphalerite by chalcopyrite and cross-cutting veinlets of pyrite may represent a later episode of sulphide deposition. Trace acanthite and electrum probably formed by exsolution from their galena host.

Later alteration in silicate skarn rocks possibly accompanied sulphide introduction and involved minor alteration of hedenbergite to magnetite and hydrogrossular, as well as the formation of calcite, hydrogrossular and quartz-hematite veins. Chloritic alteration of magnetite-grossular rocks may also have occurred at this stage.

Exposure and surface weathering of the deposit possibly commenced in the Late Tertiary (cf. Ollier and Brown, 1975; Ruxton and Taylor, 1982) and resulted in extensive leaching and oxidation of the more porous and chemically unstable parts of the skarn. This produced the vugs and pipes containing stalactitic concentrations and drusy coatings of the various secondary minerals. Coatings and fracture-fillings in massive magnetite and sulphide-poor rocks indicate

Fig. 13. Tabular hemimorphite crystals to 0.8 mm, from hemimorphite-rich pipe. J. Caldwell specimen and SEM photo.

significant precipitation from groundwater, in addition to direct replacement of sulphides. The predominance of brochantite and linarite as the main secondary copper minerals, together with the limited occurrence of malachite and apparent absence of azurite probably reflect somewhat unusual chemical conditions in the oxidized zone. Lack of azurite suggests a limited carbonate activity during weathering, and this would also account for the abundance of brochantite. Precipitation of malachite can occur under atmospheric CO_2 activity but requires neutral to weakly alkaline conditions (pH 7-8; Vink, 1986). The main weathering reactions in the gossan involved major oxidation of magnetite and more limited sulphate formation from the breakdown of less abundant sulphides. Oxidation of Fe^{2+}, contained in magnetite, to Fe^{3+} in hematite followed by hydrolosis would tend to increase the acidity (decrease the pH). Low pH values could be maintained in magnetite-rich parts of the deposit due to the limited availability of silicates and carbonates to buffer the environment to higher pH. This would restrict precipitation of malachite and favour deposition of sulphates such as brochantite and linarite.

Supergene enrichment of primary sulphides below the oxidized zone appears to have been very limited at Paddy's River. Very minor covellite, chalcocite and digenite are the only supergene sulphides that have been recognized. The restricted occurrence of pyrite, for generating excess sulphate and sulphuric acid during oxidation, and possibly the ground water conditions at the site may have contributed to this limited supergene alteration.

CONCLUSIONS

The mineralogically zoned, replacement skarn at Paddy's River formed during high-level intrusion of the Late Silurian, Shannon's Flat Adamellite. Metasomatic fluids reacted with and replaced limestones inter-

bedded with dacitic tuffs, close to the granite contact. Magnetite and calc-silicate skarn rocks probably formed at temperatures between 500° and 600°C, under relatively oxidizing conditions. These primary skarn assemblages underwent some later alteration, possibly at lower temperature. Sulphide mineralization was introduced into the skarn to form the small lodes which have been the focus for prospecting and mining activity at the deposit.

Various secondary minerals, including base metal silicates, carbonates and sulphates, developed in gossanous material as a result of surface weathering, oxidation and precipitation from percolating ground water.

At least 28 primary, and 43 distinct secondary minerals have been identified at the deposit, not including rock-forming minerals in the surrounding tuffs and granite. A further 14 minerals have been detected in cave deposits nearby. Additional minerals probably await discovery at this interesting site.

ACKNOWLEDGEMENTS

TABLE 1: Assay data from the Paddy's River Mine, A.C.T.

wt%	1	2	3	4	5	6	7	8
Cu	1.9	0.3 (nd-0.9)	2.91	3.27	8.04	2.95	-	-
Pb	3.4	0.8 (nd-3.6)	3.08	4.00	12.15	8.01	-	-
Zn	1.1	2.6 (0.8-7.7)	11.66	8.04	6.69	6.46	-	-
Fe	-	-	-	-	-	-	69.2	70.5
Mn	-	-	-	-	-	-	-	0.39
P	-	-	-	-	-	-	-	0.10
Si	-	-	-	-	-	-	2.16	0.97
Ti	-	-	-	-	-	-	-	0.17
Bi	-	-	410	315	560	300	-	
Cd	-	-	1140	770	780	620	-	-
Mn	-	-	3320	2490	2760	2100	-	-
Sb	-	-	100	80	110	50	-	-
g/t								
Ag	7.2	72 (3-318)	174	233	1230	1100	-	-
Au	2.3	<0.3 (nd-0.6)	2.1	1.6	8.8	5.2	-	-

- = not analysed, nd = not detected
1. Average reported assay for mined ore (Cowley Copper Syndicate, NSW Dept. Mines,1909 (b), analyst unknown).
2. Average and range for assays of 26 samples collected along 39m of upper adit (Tunnel No 2, from Smith, 1963; assays by South Broken Hill Ltd).
3-6 Assays of four grab samples of lode material from dumps (samples 350-920 g, analysis by ARL arc source emission spectrograph, analyst J. Caldwell).
7. Analysis of 18 kg chip sample from surface outcrops of high grade iron ore (Smith, 1963; analysis by BMR Laboratories).
8. Analysis of 0.5 kg sample of massive magnetite (analysis by EM spectrography and wet chemistry, analyst, J. Caldwell).

TABLE 2

**Minerals identified at the Paddy's River ⬤le,
associated satellite skarns and nearby caves.
(Numbers refer to techniques used in identification.)**

PRIMARY MINERALS		Carbonates		Goethite	1,2	Zinc Sulphates	2,4,
Silicates		Calcite	1,2	Hematite	1,2		5
Actinolite	1,2,3	Dolomite	2,4	Pyrolusite	2	Phosphates	
Andradite	1,2,3			'Sturtite'	2,3,4	Pyromorphite	2,4
Chlorite (IIB)	1,2,3	Sulphates		Todorokite	2		
Clinochlore	1,2,3	Barite	2			Arsenate	
Clinozoisite	1,2,3			Halides		Scorodite	4,5
Dannemorite	1,2,5	SECONDARY MINERALS		Cerargyrite	2,4		
Diopside	1,2,3					Cave Minerals	
Epidote	1,2,3	Native Elements		Carbonates		Alunite	2,4
Gonyerite	2,3,6	Silver	1,4	Aurichalcite	2,4	Aragonite	2,4
Grossular	1,2,4	Sulphur	1,5	Cerussite	2,5	Berlinite	2,4
Hedenbergite	1,2,5			Hydrozincite	2,5	Collophane	2,4
Hydrogrossular	1,2	Silicates		Kutnohorite	2,5	Crandallite	2,5
Leuchtenbergite	2,5	Chamosite	1,2,3	Malachite	2,4	Dahllite	2,4
Quartz	1,2	Chrysocolla	1	Siderite	1,4	Francoanellite	2,4
Talc	2	Halloysite	2,6	Smithsonite	2	Gypsum	2
Thuringite	1,2,4	Hemimorphite	1,2,6			Huntite	2
'Uralite'	1,2	Hyalite	1,2,4	Sulphates		Hydromagnesite	2
		Inesite	2,5	Anglesite	2	Leucophosphite	2,5
Sulphides		Nontronite	2,5	Bianchite	2,4	Nesquehonite	2
Acanthite	1,2	Sauconite	2,4	Brochantite	1,2,6	Niter	2
Arsenopyrite	1,5	Zincsilite	2,4	Caledonite	1,2	Nitrocalcite	2,4
Bornite	2			Chalcanthite	2,4		
Chalcopyrite	1,2,3	Supergene Sulphides		Coplapite	2,4	1 = optical microsco-	
Galena	1,2,4	Chalcocite	1,2	Goslarite	2,4	py	
Pyrite	1,2	Covellite	1	Gypsum	2,4	2 = X-ray diffraction	
Sphalerite	1,2,3	Digenite	1,2,5	Jarosite	2	3 = X-ray fluorescence	
				Langite	2	4 = wet chemical anal-	
Oxides		Oxides, Hydroxides		Linarite	1,2,4	ysis	
Magnetite	1,2,4	Carphosiderite	2,3,6	Pickeringite	2	5 = SEM - EDAX	
Specular Hematite	1,2	Ferrihydrite	4	Rozenite	2,4	6 = SEM - morphology	

All photographs by P. Millsteed. All samples collected by G. Morvell.

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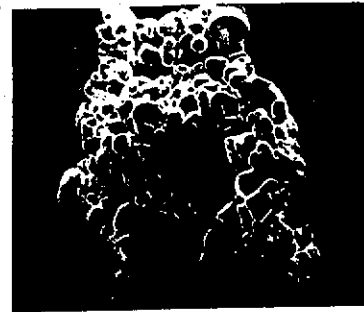3 Oak Tree Road, Bawtry
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Fig. 14. Globular native silver with spheroidal forms to 20μ. G. Morvell specimen, J. Caldwell SEM photo.

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